Surface and material properties governing ultrahigh vacuum

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Outline

Ultrahigh vacuum
Physisorption vs. chemisorption
Simple molecules on surfaces
Hydrogen: adsorption and absorption
Conclusions

Atmospheric pressure conditions

air composition

GAS	SYMBOL	PERCENT BY VOLUME
Nitrogen	N_2	78
Oxygen	O_2	21
Argon	Ar	0.93
Carbon Dioxide	CO_2	0.03
Neon	Ne	0.0018
Helium	He	0.0005
Krypton	Kr	0.0001
Hydrogen	H_2	0.00005
Xenon	Xe	0.0000087
Water	H_2O	Variable

For air-N_2 (M=28) at 295 K

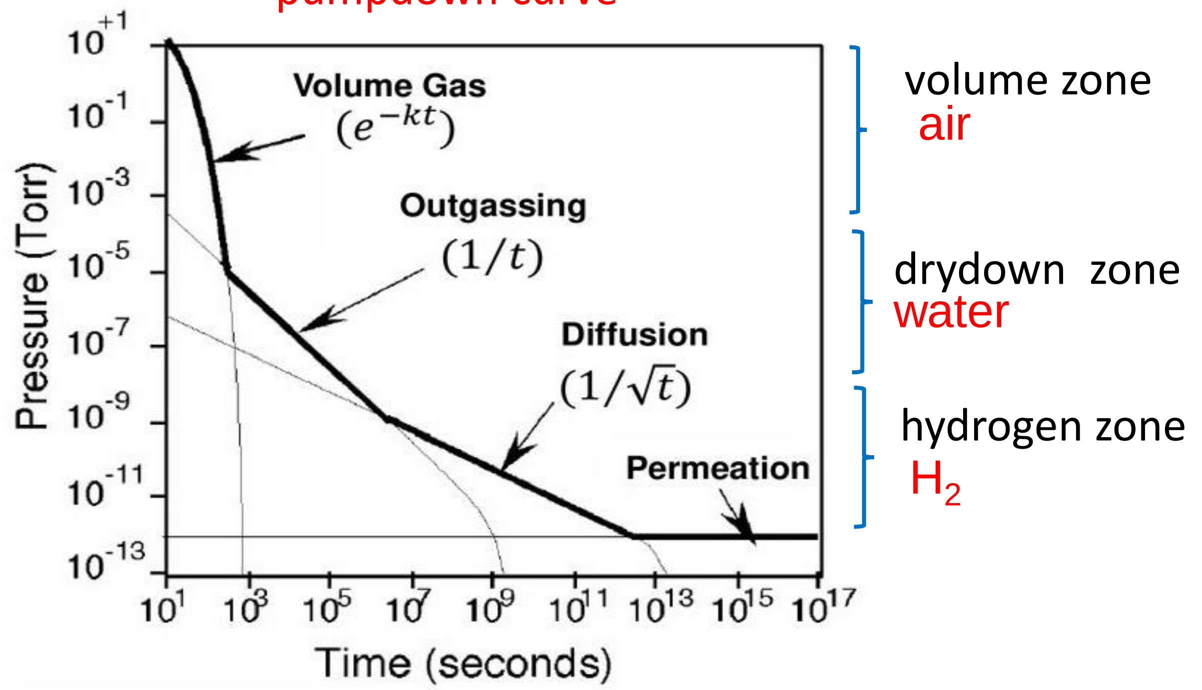
P (mbar)	n (litre^{-1})	λ	J (cm^{-2}s^{-1})	t_{ML} (s)
1000	2.5×10^{22}	66 nm	2.9×10^{23}	2.5×10^{-9}

λ (mean free path): average distance a gas molecule travels before it collides with another gas molecule

t_{ML} time needed for the adsorption of a complete monolayer

Pump-down curve

pumpdown curve



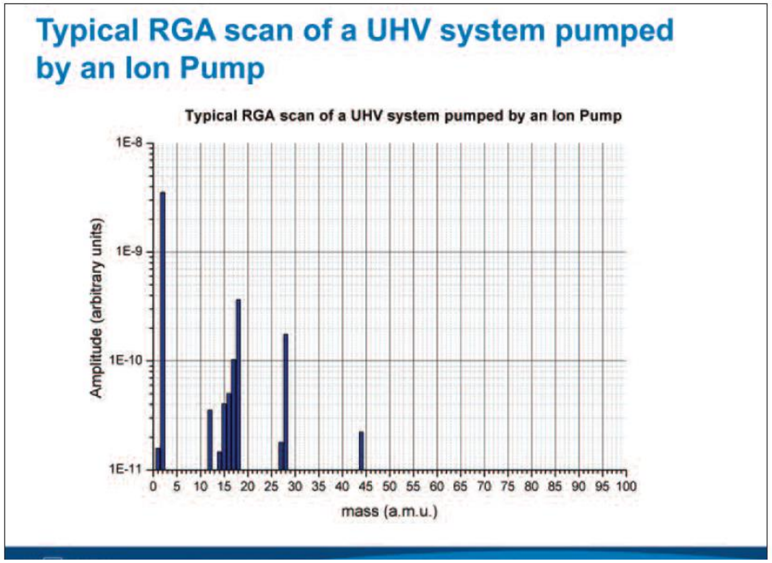
outgassing: release of gases accumulated on any internal surface. Can be accelerated by baking

diffusion: gas particles present in the vessel walls which are released into the system

permeation: gas migrating through the velles walls from atmosphere and released into the system

The ultimate pressure is limited by the diffusion/permeation of hydrogen

UHV conditions



UHV →

For air-N_2 (M=28) at 295 K

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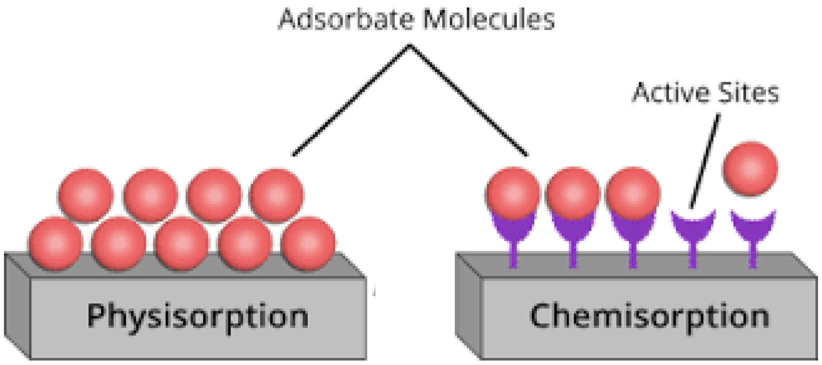
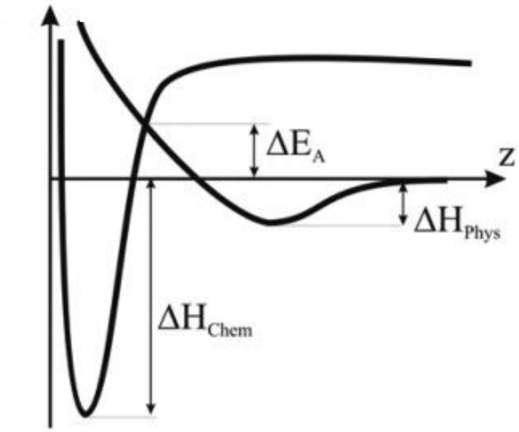
1000	2.5×10^{22}	66 nm	2.9×10^{23}	2.5×10^{-9}
1	2.5×10^{19}	66 μm	2.9×10^{20}	2.5×10^{-6}
10^{-3}	2.5×10^{16}	66 mm	2.9×10^{17}	2.5×10^{-3}
10^{-6}	2.5×10^{13}	66 m	2.9×10^{14}	2.5
10^{-10}	2.5×10^{9}	660 km	2.9×10^{10}	2.5×10^{4}

https://www.agilent.com/cs/library/training/Public/UHV_Seminar_Handbook.pdf

In UHV $N_{vellel\ walls}/N_{vessel\ volume} \sim 500$: collisions between gas particles and wall dominate

Physisorption vs. chemisorption





potential energy of a molecule with distance from a surface

physisorption

binding energy is very weak (~10–300 meV) and non-localized

the adsorption forces include London Forces, dipole-dipole attractions (van der Walls forces) minimal perturbation of the electronic states

no activation energy is involved

adsorbates form multilayers

chemisorption

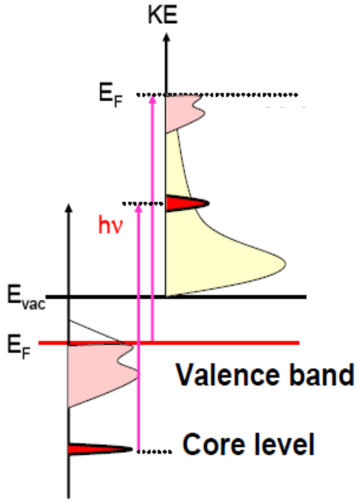
binding energy of 1–10 eV and localized chemical specificity

changes in the electronic states chemical bonding (ionic or covalent)

often involves an activation energy

adsorbates form one monolayer
strong interaction between adsorbates

X-ray photoelectron spectroscopy (XPS)

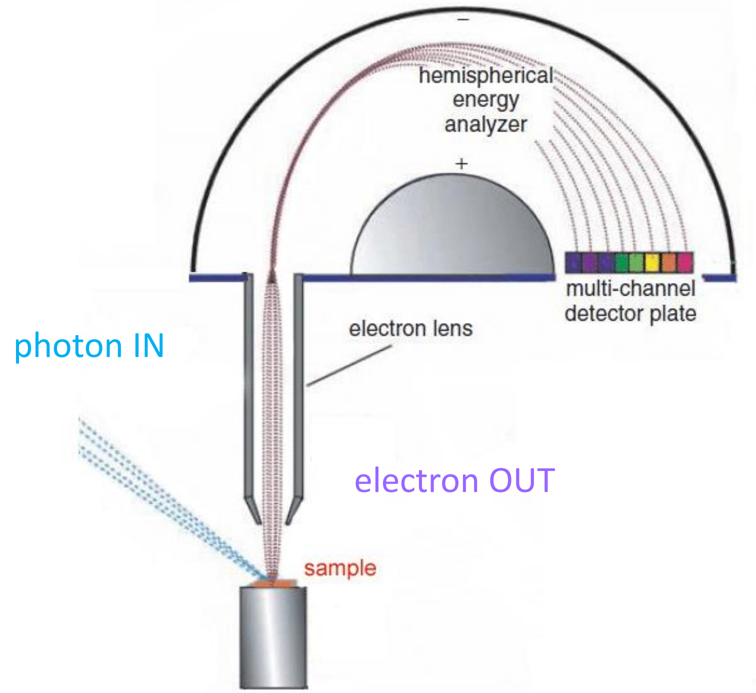


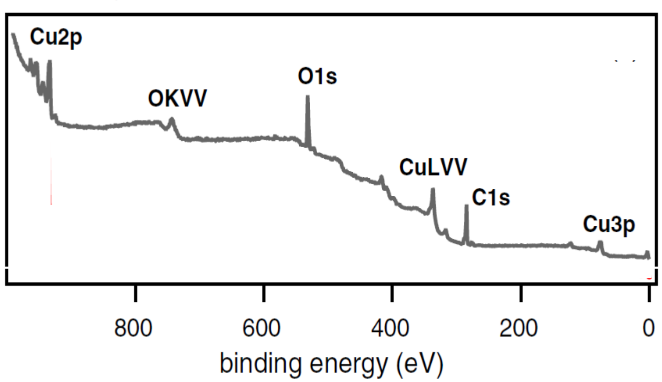
KE=hv-BE-φ

KE: kinetic energy

φ: work function

BE: binding energy





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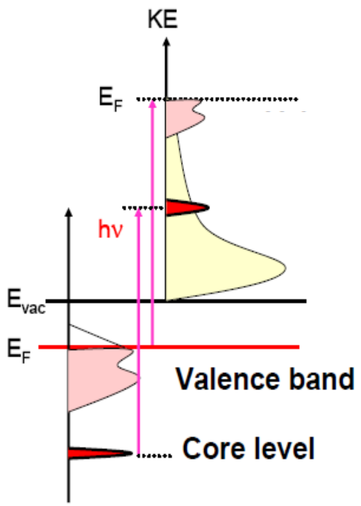
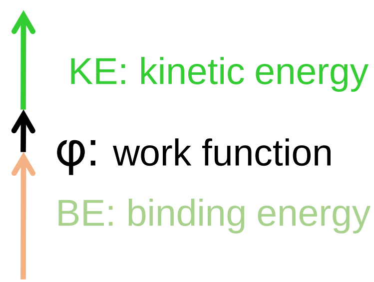
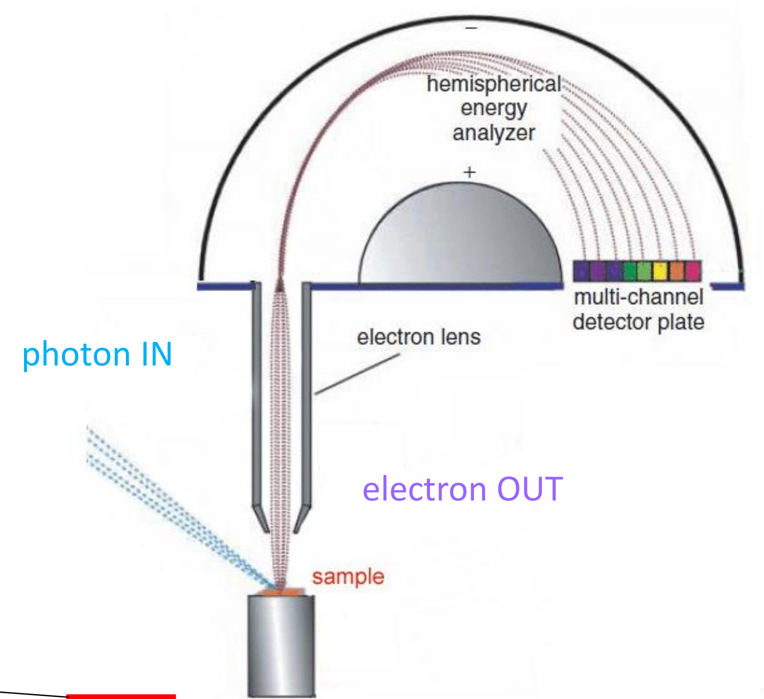
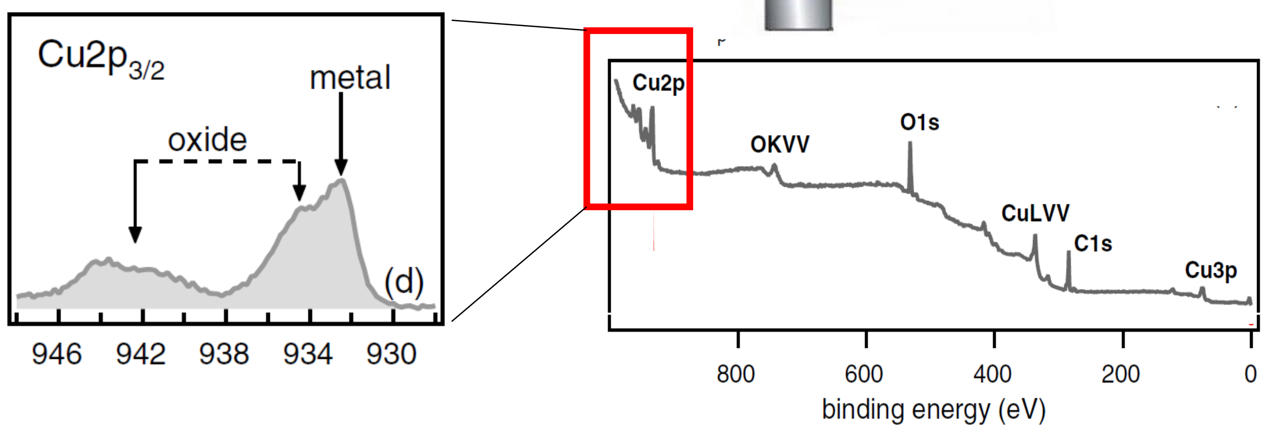


$$KE=h\nu-BE-\varphi$$

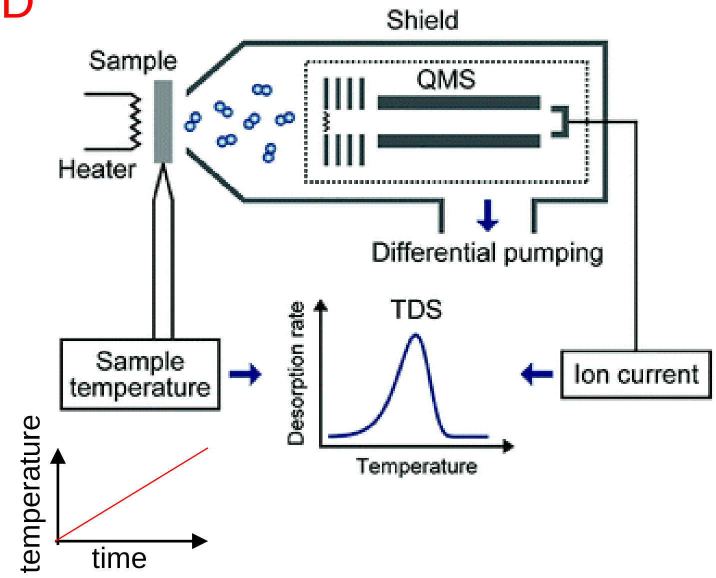


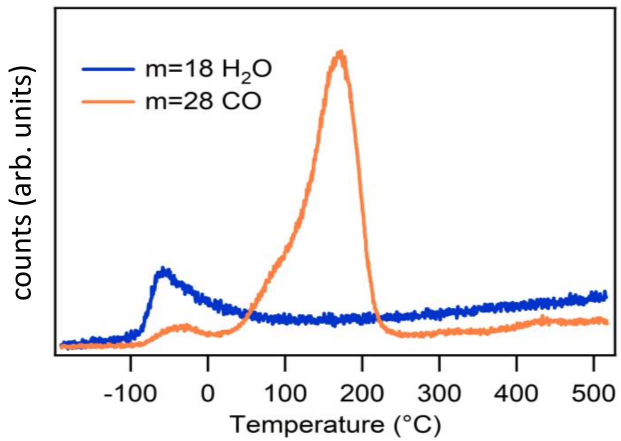




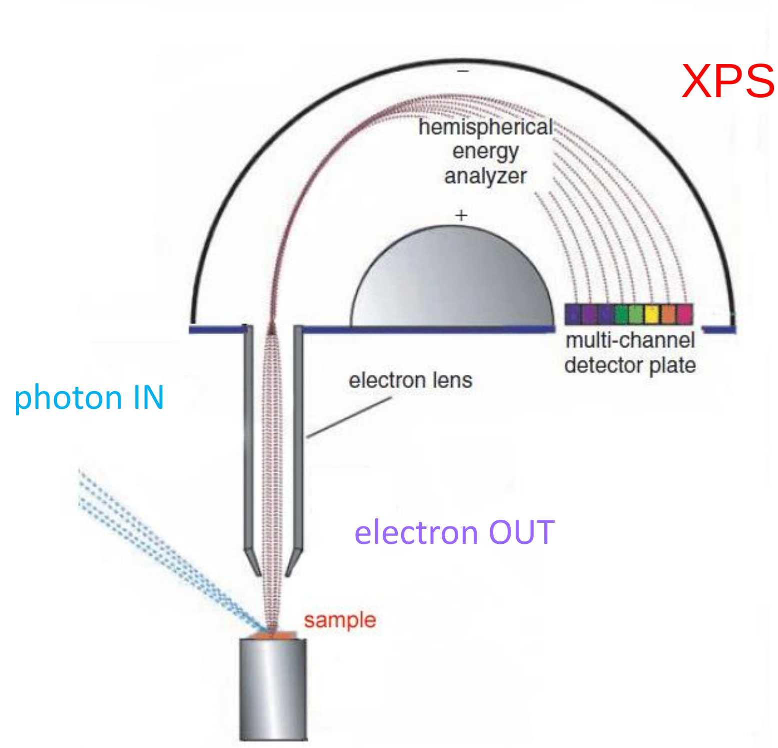
Thermal programmed desorption (TPD)

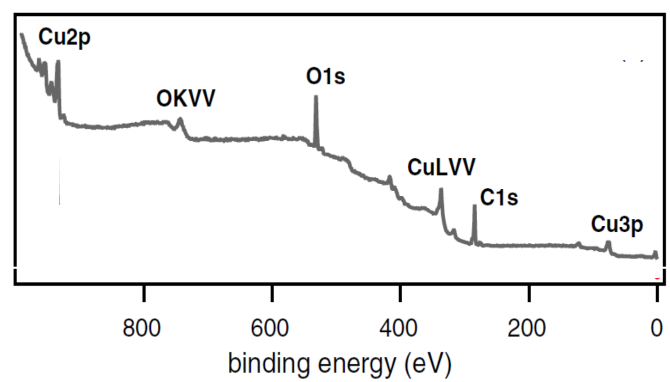
TPD





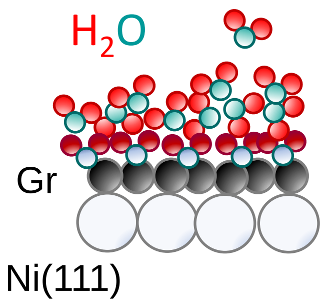
XPS

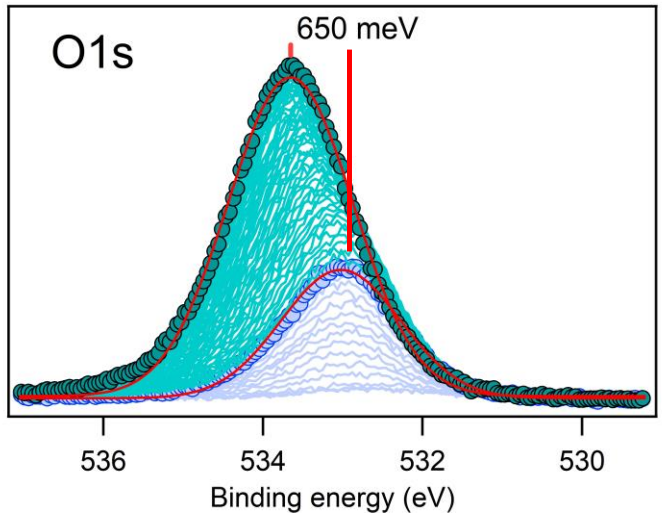


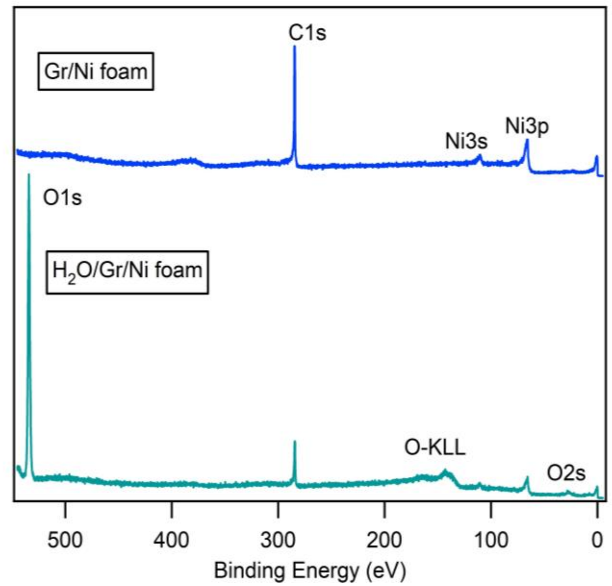


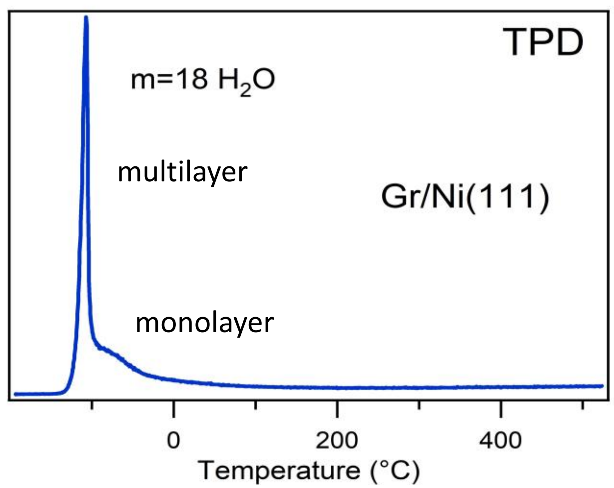
Physisorption of water

-190 °C, p=5x10^{-10} mbar, 120'









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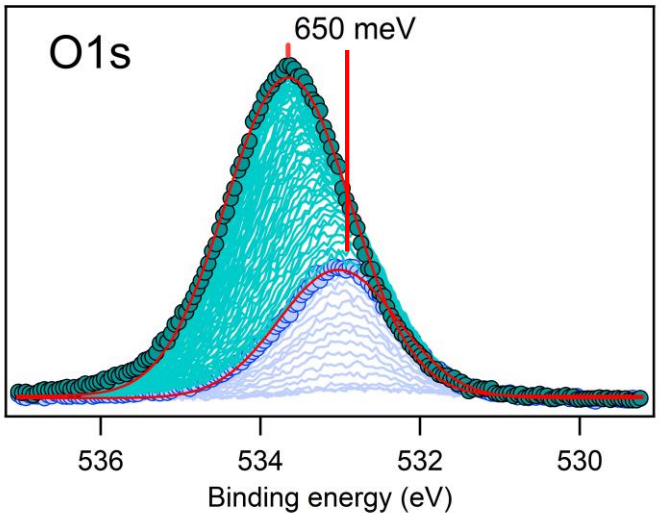
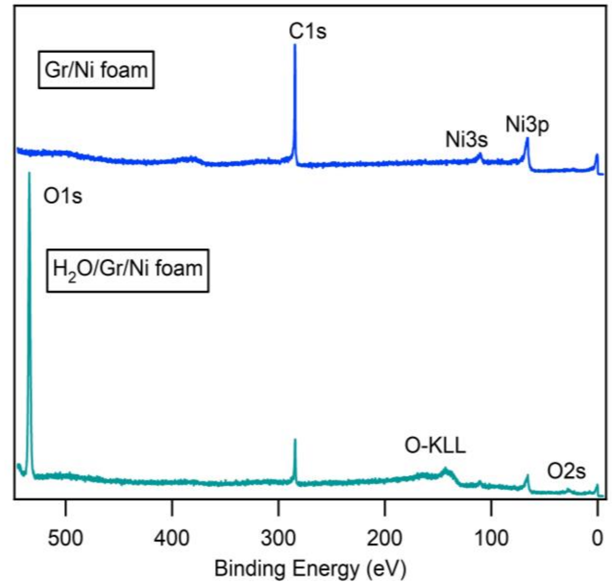
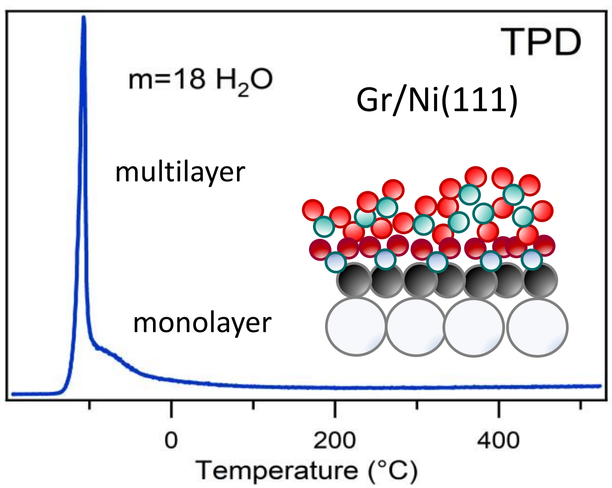
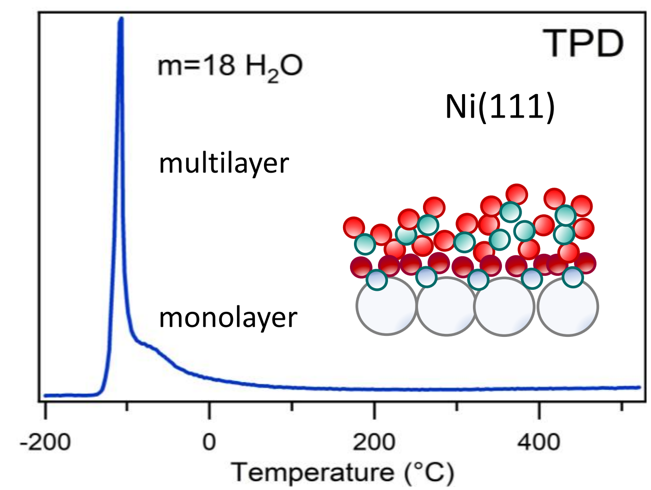




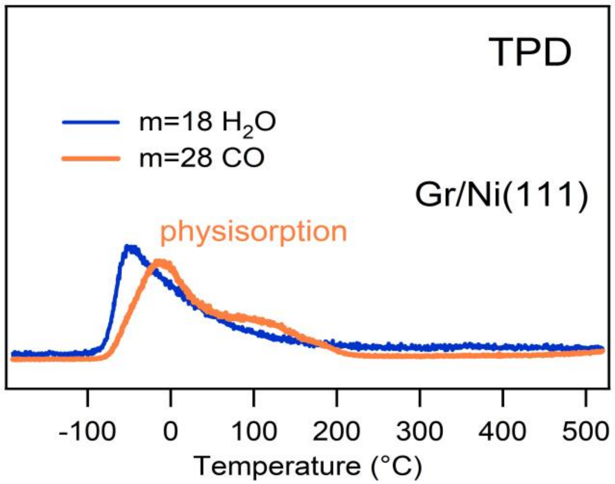


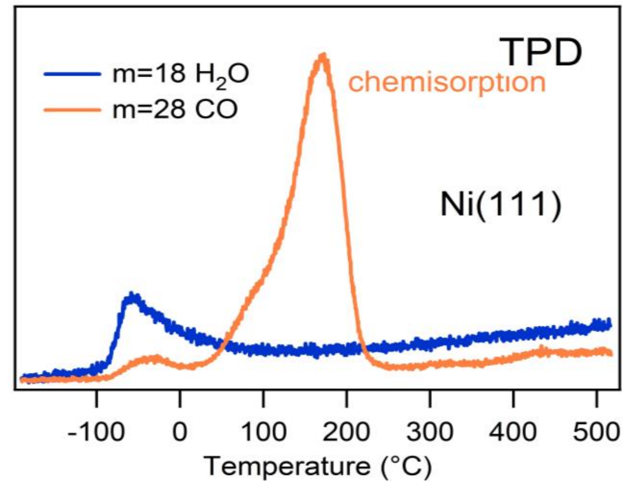


Physisorption and chemisorption

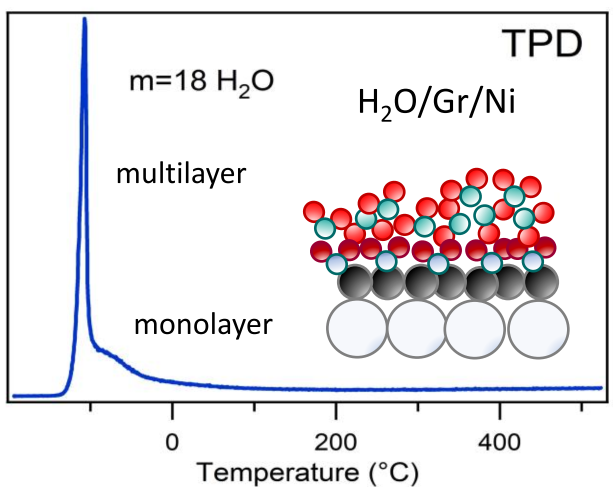
p=5x10^{-10} mbar, 120’

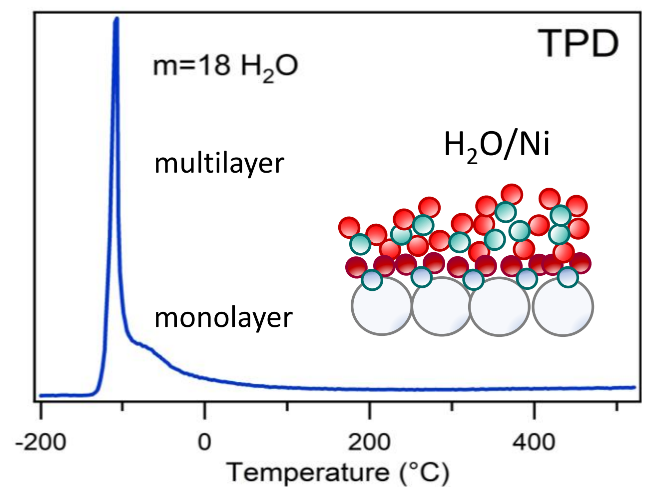
-100 °C





-190 °C

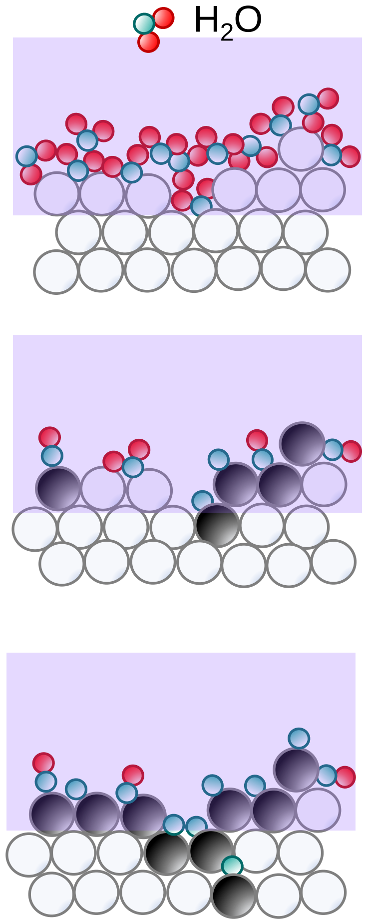




Radiation induced surface processes

synchrotron radiation

hyperthermal electrons



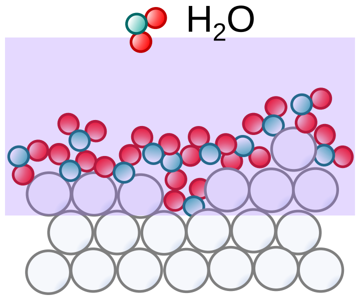
desorption dissociation

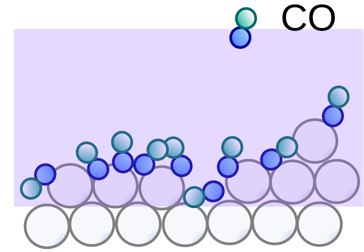
oxide formation

Radiation induced surface processes

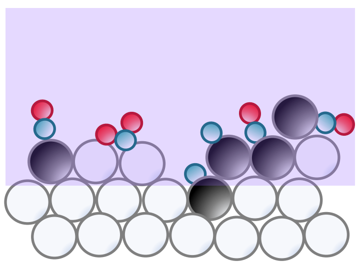
synchrotron
radiation

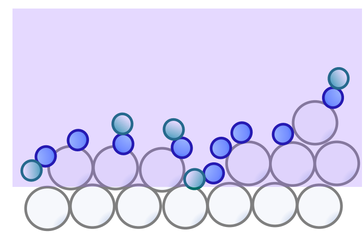
hyperthermal
electrons





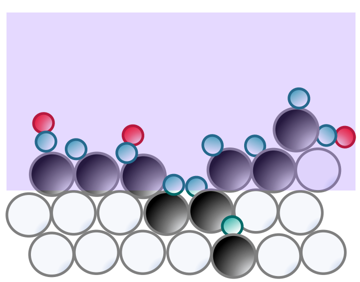
desorption
dissociation

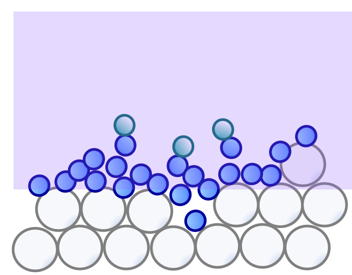




desorption
dissociation

oxide
formation



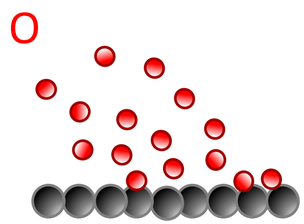


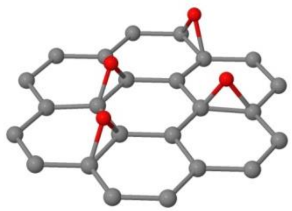
C layer growth

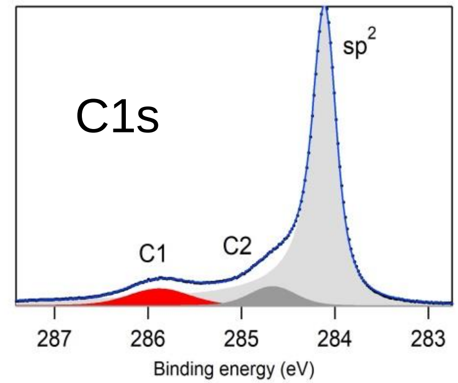
CO is a precursor

scrubbing rate depends on composition of the background pressure, nature and chemical state of the metal wall

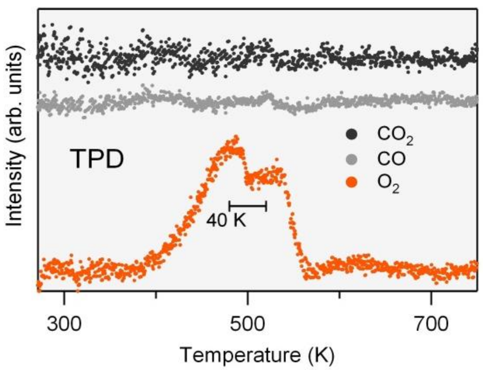
Oxygen chemisorption on graphene

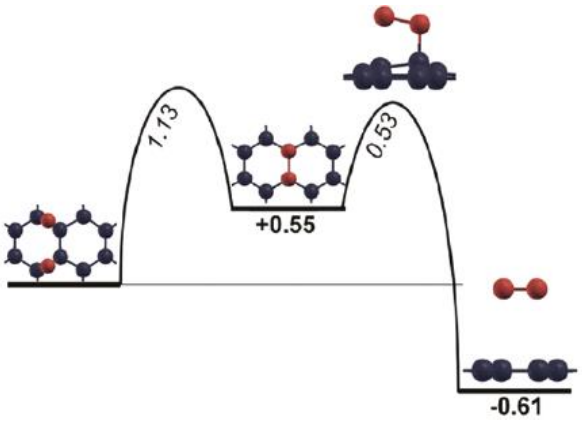






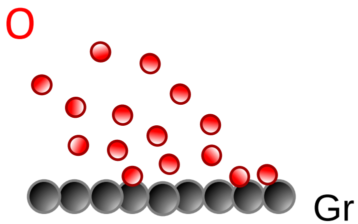
E(des) 1.21±0.02 eV

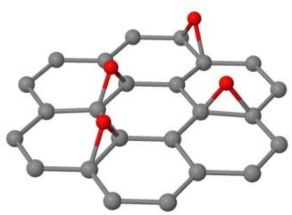


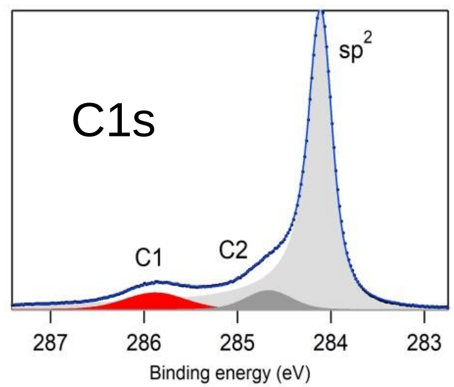


R. Larciprete et al. JACS 133 (2011) 17315

Oxygen chemisorption on graphene







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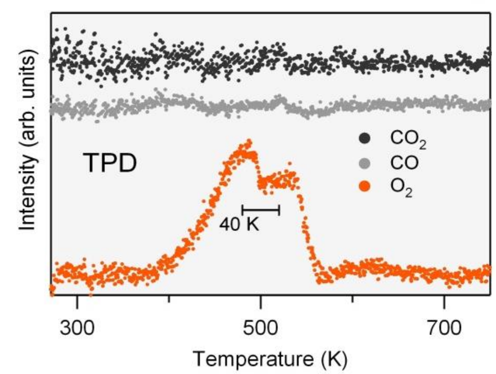
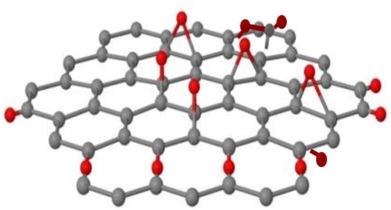
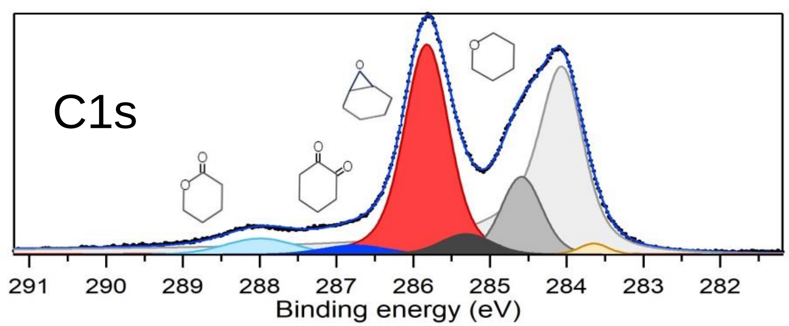
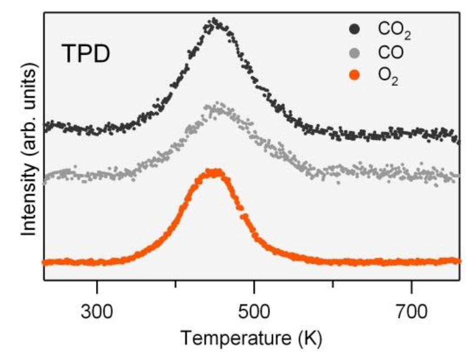




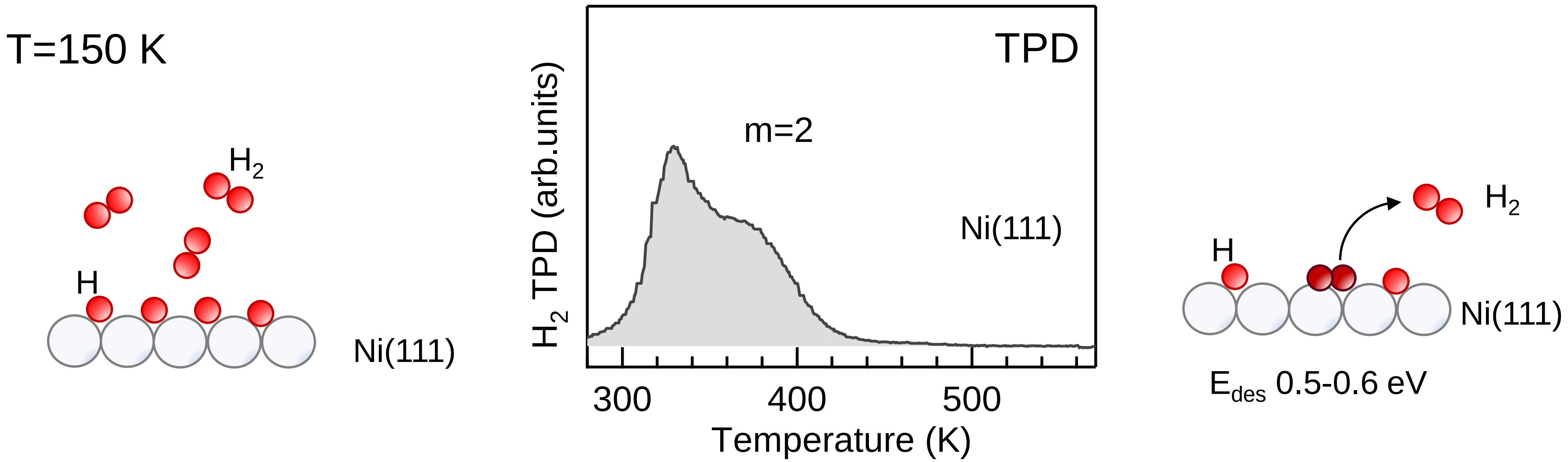




E(des) = 1.19-1.21 eV

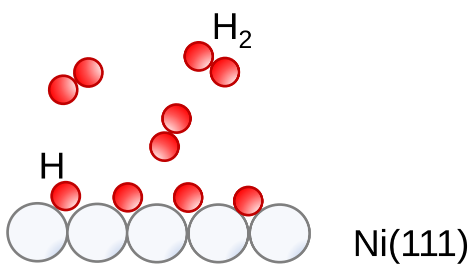
R. Larciprete et al. JACS 133 (2011) 17315

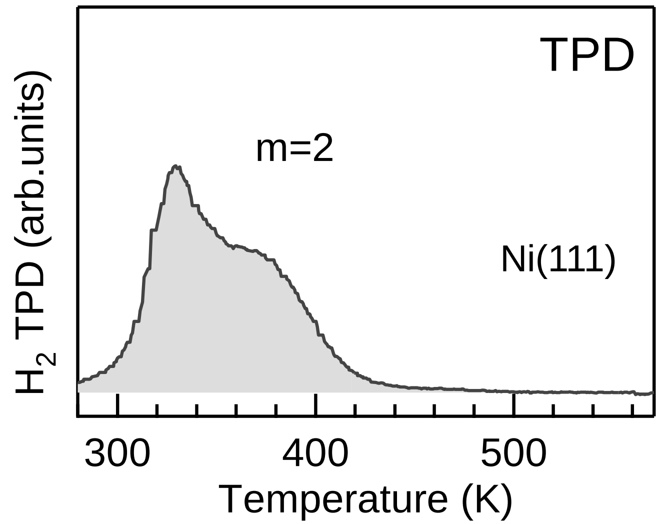
Dissociative chemisorption of H_2

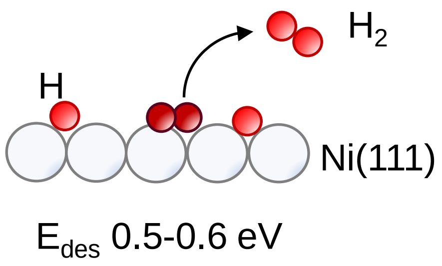


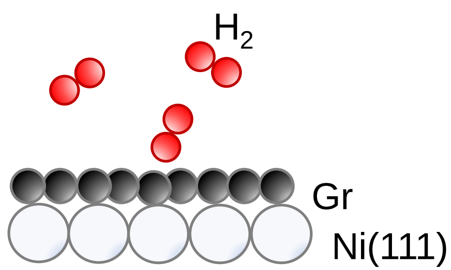
Dissociative chemisorption of H_2

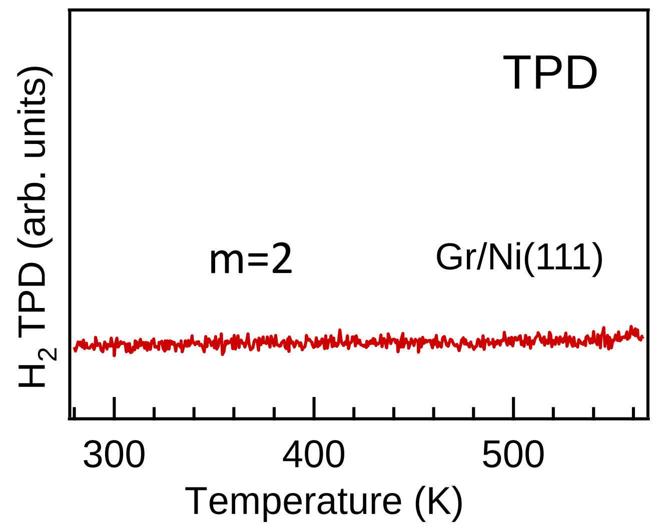
T=150 K





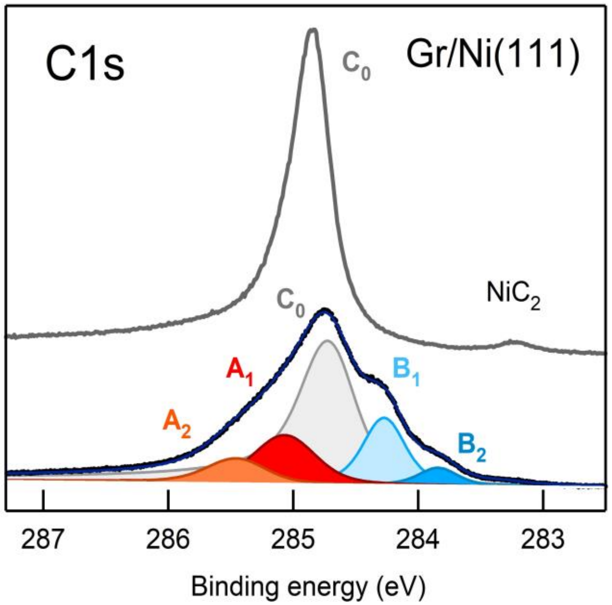


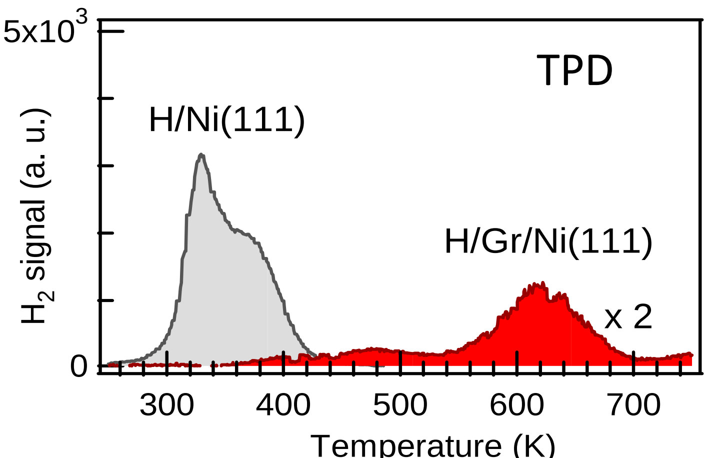




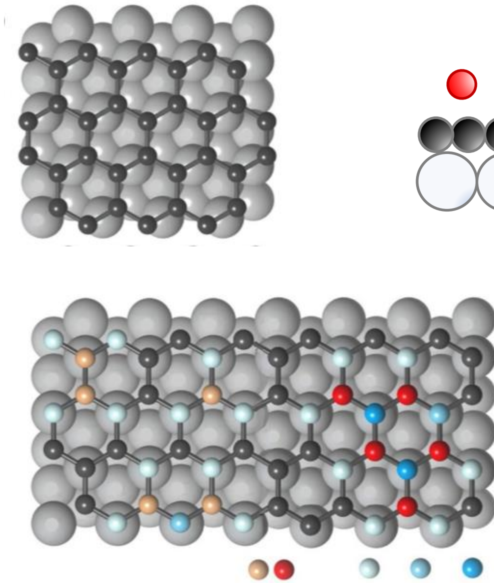
Chemisorption of H atoms on graphene/Ni(111)

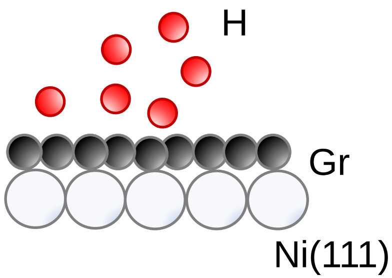
T=300 K





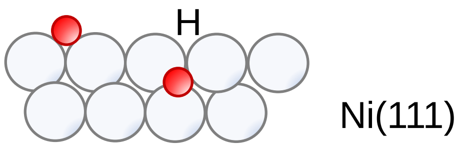
E_{des} ~1.6 eV

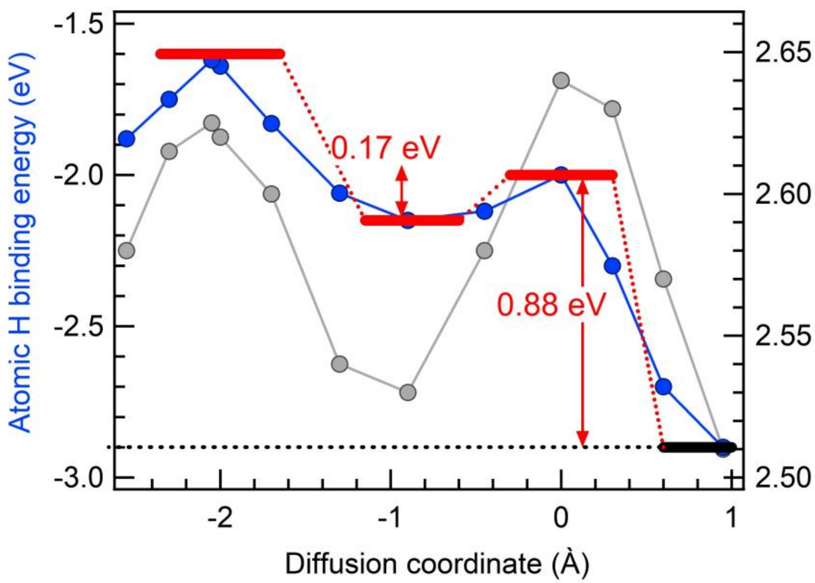




Lizzit et al. ACS Nano 13 (2019) 1838

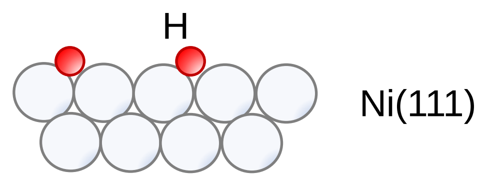
H/Ni(111): diffusion in the bulk

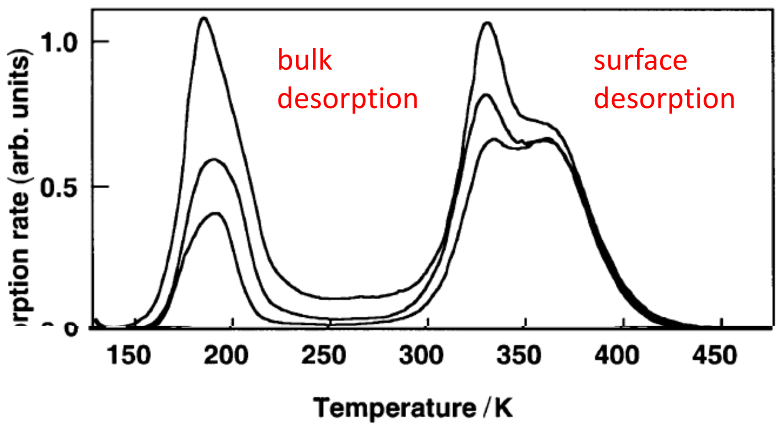




Greeley et al. Surf. Sci. 540 (2003) 215

Shirazi et al. Phys.Chem.Chem.Phys. 19 (2017) 19150



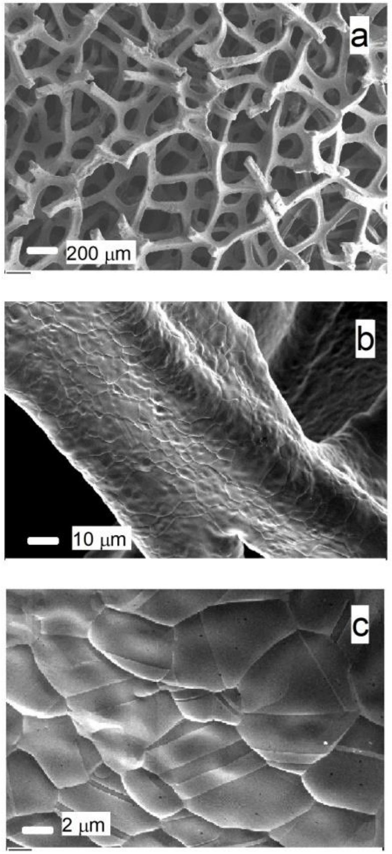


Wright et al Faraday Discuss. 117 (2000) 133

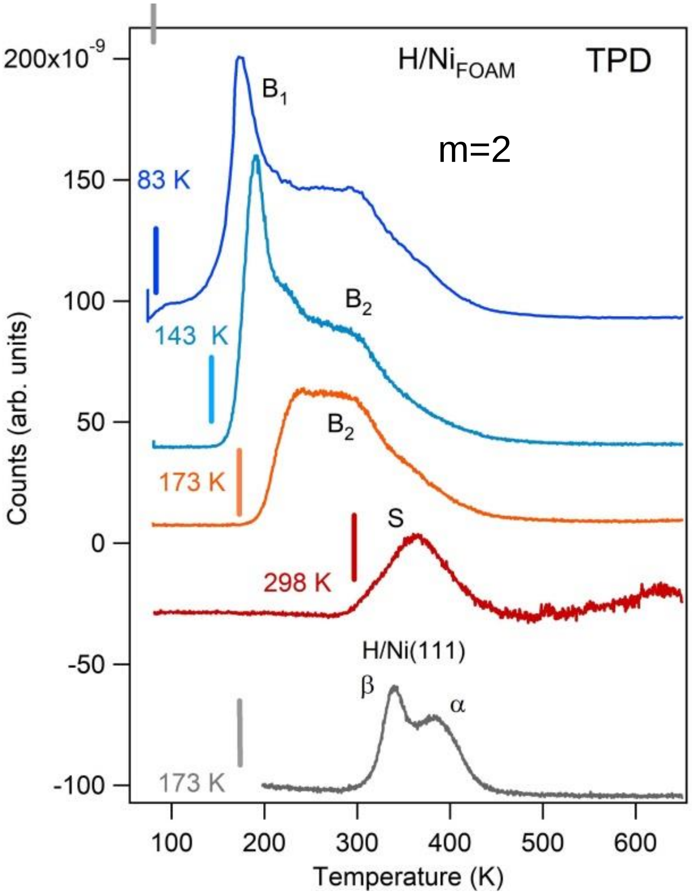
Johnson et al PRL 67 (1991) 927

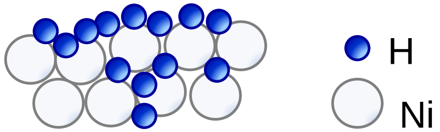
H/Ni foam: diffusion in the bulk

Ni foam



porosity 95%, purity 99.5%
thickness 1.6 mm





Petrone et al. Carbon 199 (2022) 357

CONCLUSIONS

Even in ultra-high vacuum regime several surface reactions occur between the components of the residual pressure and the internal vessel surfaces.

The adsorption of atoms and molecules occurs through physisorption and chemisorption processes. Physical agents (temperature, radiation, …) might determine desorption and/or dissociation of the adsorbates.

Physisorbed adsorbates in dynamical equilibrium with the residual pressure might compromise the functional properties of devices (optics, …SEY, NEG) and determine pressure bursts when suddenly desorbed by physical stresses.

Chemical bonding of adsorbates to metal walls determines compound formation (oxides, C film,……→ *scrubbing*) which permanently modify the surface composition.

Surface reactivity might be mitigated by the presence of a carbon layer.

Studying ordered systems makes understanding easier and provides fundamental knowledge. Adding disorder and defects of real systems widens the manifold of possible reactions and modifies the energetics of the interactions.

Knowing the nature and the rate of the surface reactions which can occur in ultra-high and even in extreme vacuum are at the basis of the pressure and operation stability in particle accelerators and other critical environments**.**

Thanks for your attention!